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A multidisciplinary approach to the study of underwater artefacts: the case of a *Tritone Barbato* marble statue (Grotta Azzurra, Island of Capri, Naples)

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Abstract

A multidisciplinary investigation was carried out in order to study the sculpture materials, state of preservation and provenance of a marble statue representing a *Tritone Barbato*, together with what is believed to be its base. Both items were recovered during the 1960s from an underwater environment in the *Grotta Azzurra*, Capri, southern Italy. Together with other statues, these archaeological finds were a decorative element in the *nymphaeum* (grotto) associated with a maritime imperial villa dating back to the Roman period, attributed to Emperor Tiberius. Diagnostic analysis represents an essential tool for the selection of an appropriate cleaning procedure, since the latter is an irreversible process. For this reason, a study of the nature and extent of degradation was conducted via optical and scanning electron microscopy. In addition, petrographic analysis, oxygen and strontium isotopic ratios, evaluation of maximum grain size (MGS) and determination of Mn content made it possible to determine textural characteristics, as well as to formulate some hypotheses regarding the marble's provenance. The results point to Carrara as a potential raw material source and indicate that the two marble items belong to the same artefact.

Key words: bioerosion; deterioration; diagnostic; marble; provenance; underwater artefacts.

Introduction

In recent years, interest in studying degradation and alteration phenomena in underwater finds has increased considerably. Researchers now recognise the importance both of understanding how archaeological objects degrade during long exposure to water (Petriaggi, 2002) and of finding suitable methods for their cleaning and conservation (Crisci et al., 2010).

The most important problem facing submerged

archaeological artefacts is obviously physical and chemical damage (Pearson, 1987). Submarine weathering may take several different forms, including oxidation caused by dissolved oxygen, biological colonisation by micro- and macro-organisms (biofouling) and ionic corrosion (Parrini, 1986).

Defined as the undesirable accumulation of microorganisms, algae and/or animals on submerged structures, marine biofouling can be roughly divided into two different categories: microfouling (by bacteria) and macrofouling (e.g. macroalgae, barnacles, mussels, tubeworms and bryozoans). The organisms comprising these two groups are often found together, forming the fouling community (Fay et al., 2011).

Diagnostic analysis is very important not only in choosing an appropriate restoration strategy, but also in solving provenance issues. A complete understanding of the chemical nature and structure of encrustations is essential for the conservator, since the cleaning procedure is an irreversible process and an incorrect choice could result in irrecoverable damage. Different degradation phases are dominated by compounds such as calcareous concretions, encrustations and alumino-silicate crusts, as well as other inorganic species (iron, manganese, copper and black sulphides) or organic stains (Casaletto et al., 2008).

Provenance analysis of stone materials is a crucial component of various kinds of research, including the reconstruction of trade routes, the purchase of base material for restoration and the testing of compatibility between materials and conservation practices.

As one of the most aesthetically valuable stones used both in antiquity and in recent times for architectural and decorative work, white marbles have proven extremely popular for employment in cultural heritage programmes.

During the Roman era, blocks of marble were transported far from quarries and are thus found at archaeological sites throughout the Mediterranean. Given the physical heterogeneity of marble even within the same quarry, especially in the case of those active for hundreds of years, it is often difficult to distinguish the provenance of varieties of marble via visual analysis alone (Siegesmund et al., 2010).

As marble provenance has been studied since the 1950s by means of petrographic, geochemical and isotopic techniques, it has become increasingly clear that the use of a single method does not enable conclusive identification of the most famous marbles used in antiquity; recent investigations thus typically employ a combination of methods to achieve more promising results (Lazzarini, 2004; La Russa et al., 2010; Miriello et al., 2010).

In the present multidisciplinary study, several diagnostic analyses were carried out in order to characterise alteration and degradation forms and to determine the provenance of the sculpture material of two archaeological finds: a marble sculpture representing a *Tritone Barbato* and a marble monolith, likely the statue base. Both finds were recovered from the underwater archaeological site known as the “Grotta Azzurra” on Capri, an island located on the south side of the Gulf of Naples (southern Italy).

Several microscopic techniques including stereomicroscopy, transmitted light optical microscopy and scanning electron microscopy (SEM) were employed to study superficial colonisation, bioerosion phenomena, interactions with the marble substrate and textural characteristics. Finally, in order to determine the provenance of the two marble artefacts, petrographic analysis was performed to calculate the maximum grain size (MGS) of calcite crystals, an important marker when formulating hypotheses regarding marble provenance. A combination of inductively-coupled plasma mass spectrometry and laser ablation (LA- ICP/MS) was also used to determine marble Mn content, while analysis of $^{87}Sr/^{86}Sr$, O and C isotopic

ratios was carried out via mass spectrometry. All of these analytical chemistry techniques represent important tools for the distinction of different marble sources (Lazzarini, 2004).

Archaeological context and macroscopic description of the *Tritone Barbato* sculpture

As first reported by De Franciscis (1964), the statue of *Tritone Barbato* was discovered, together with its base, in the *Grotta Azzurra* cave in 1964 (Figure 1). Located in the village of Anacapri on the northwestern side of the island of Capri (Naples), the cave forms part a karstic system of which only the first chamber is accessible today. Above the cave there is a Roman villa dating back to the Emperor Tiberius, built between 27 and 37 B.C. The cave was probably used as a nymphaeum in Roman times, with this assumption confirmed after the retrieval of different complete statues, as well as statue and architectural fragments. All of these archaeological finds are currently being exhibited in the museum of Casa Rossa (Anacapri) and in the rooms of the *Soprintendenza Speciale per i Beni archeologici di Napoli e Pompei* in Naples and Anacapri.

The present study is framed within the research project titled *"Grotta Azzurra - Over the blue: hypothesis of valorisation and study of the state of conservation of the marble statues*" (Ricci et al., 2011), with the permission and collaboration of the Soprintendenza Speciale per i Beni Archeologici di Napoli e Pompei. A number of ISCR (Istituto Superiore per la Conservazione ed il Restauro) experts are also currently involved in the conservation assessment of the marble statues that formed part of the sculptural furniture of the nymphaeum, as well as in the biological study of artefact damage due to their location in a typical cave environment.

Both the 1.50 m tall sculpture and its base (about 50 cm) are constructed of white marble (Figure 2). According to archaeological evidence, the two items are part of the same artefact. All surfaces of both items are characterised by strong degradation phenomena, mainly due to biological activity. On a macroscopic scale, white and yellow deposits, probably related to the presence of epilithic sponges, can be observed, in addition to encrustations formed due to the growth of serpulids, bryozoans, barnacles and molluscs. Finally, numerous holes and pitting produced by endolithic bivalves and sponges are likely responsible for the significant decohesion phenomena visible.

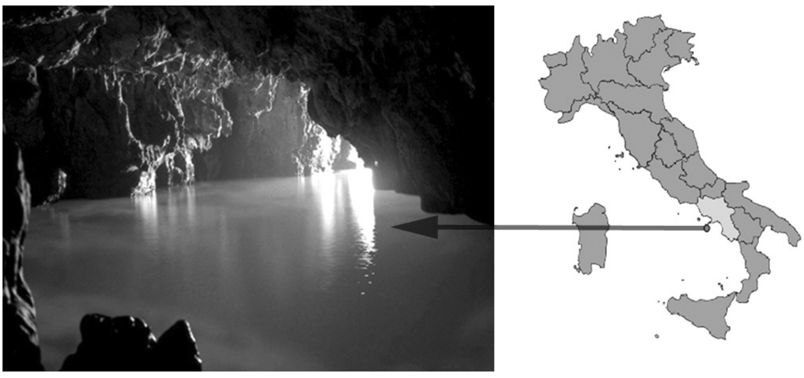

Figure 1. The Grotta Azzurra, Capri Island (southern Italy).

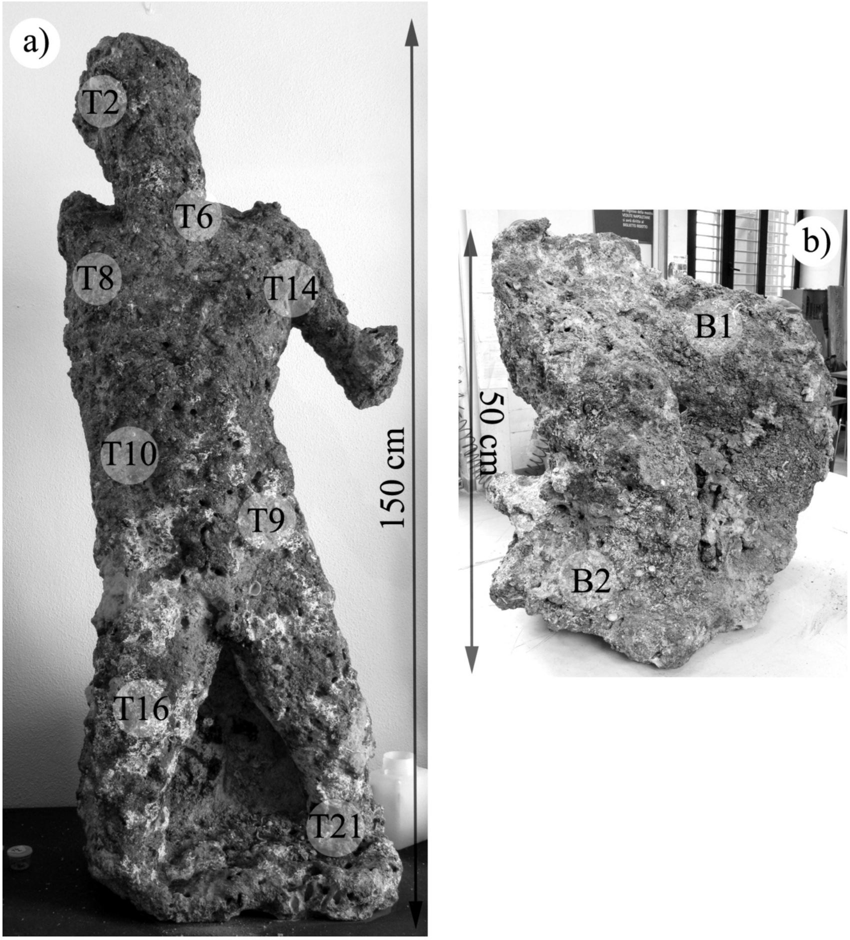

Figure 2. Sampling from the marble statue a), and the base b).

Experimental

Ten samples of stone material, including their degradation products, were taken from different points on the statue and base (Figure 2); the size of these samples never exceeded 3 cm. Stainless steel tools and surgical lancets were used, with the sampling criteria including the following: a good state of substrate aggregation, availability and representativeness of the main alteration and degradation products.

For complete characterisation of the stone materials and alteration/degradation products, several analyses were carried out:

a) Polarised light optical microscopy of thin sections and stratigraphic thin sections, in order to study the mineral and textural characteristics of samples, including their superficial layers. For this purpose an Axioskope 40 (Zeiss Axiolab) microscope was used; maximum grain size (MGS) (Moens et al., 1988) values were determined by measuring the largest calcite grain found within thin sections of the same item;

b) Morphological analysis was carried out on

fragments using an FEI Quanta 200F Philips scanning electron microscope, coupled with EDS. All SEM-EDS analyses were conducted with an acceleration voltage of 20 kV and under low vacuum conditions (10^{-3} mbar pressure);

c) Mn content was measured on unaltered material via laser ablation (LA) ICP-MS; the employed equipment was an Elan DRCe (Perkin Elmer/SCIEX) connected to a New Wave UP213 solid-state Nd-YAG laser probe (213 nm). Ablation was performed with spots of 80 µm, a constant laser repetition rate of 10 Hz and a fluence of 20 J/cm^2. Data were transmitted to a PC and processed in the GLITTER software program; calibration was performed using glass reference material NIST 612-50 ppm (Pearce et al., 1997) in conjunction with internal standardisation, applying CaO concentrations (Fryer et al., 1995) from SEM-EDS analyses. In order to evaluate possible errors within each analytical sequence, determinations were also made on BCR 2G glass reference material;

d) Measurements of the stable isotopes of carbon, oxygen and $^{87}Sr/^{86}Sr$ were conducted for provenance analysis on unaltered portions of each marble sample (one analysis per sample). Isotopes were determined at the Stable Isotope Laboratories of Queen's University, Kingston (Canada); for analysis of the stable isotopes of carbon and oxygen, samples were reacted with BrF_5 at ~ 650 °C in nickel bombs, following the procedures described by Kyser et al. (1981). Analyses were then largely performed on a Deltaplus XP dual inlet isotope ratio mass spectrometer, with carbon isotopic compositions determined on a Carlo Erba Elemental Analyser coupled with a Finnigan Mat 252 isotope ratio mass spectrometer. Results are expressed in terms of the deviation δ from a conventional standard, in this case Pee Dee Belemnite, a carbonate fossil from South Carolina. Deviation values are written in terms of either $\delta^{13}C$ or $\delta^{18}O$, measured in parts per thousand and calculated as follows: δ *(‰)* = [R sample/R standard - 1] · 1,000, where R = $^{13}C/^{12}C$ or $^{18}O/^{16}O$.

$^{87}Sr/^{86}Sr$ ratios were determined using a Thermo Finnigan multi-collector ICP-MS (inductively-coupled plasma mass spectrometer) in relation to the certified standard NBS 987.

Results and discussion

Petrographically, all marble samples exhibited a similar structure, with thin section analysis revealing homogenous granoblastic and fine-grained microfabrics. Most samples showed an almost perfectly covered grain fabric with straight (largely open) grain boundaries and frequent 120° triple junctions (Figure 3a,b); the grains also presented no preferred lattice orientation. Opaque oxides and muscovite were accessory minerals.

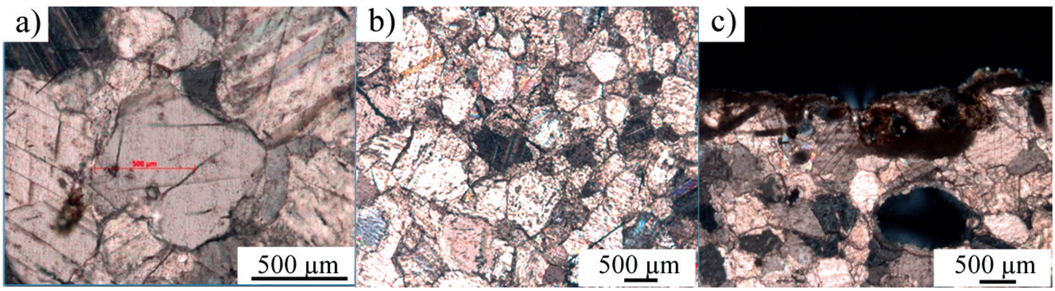

Figure 3. Polarizing light optical microscopy images taken from thin sections of the marble samples; a) Detail of the marble texture, crossed Nicols; b) Marble texture, crossed Nicols; c) Detail of outer layer, crossed Nicols.

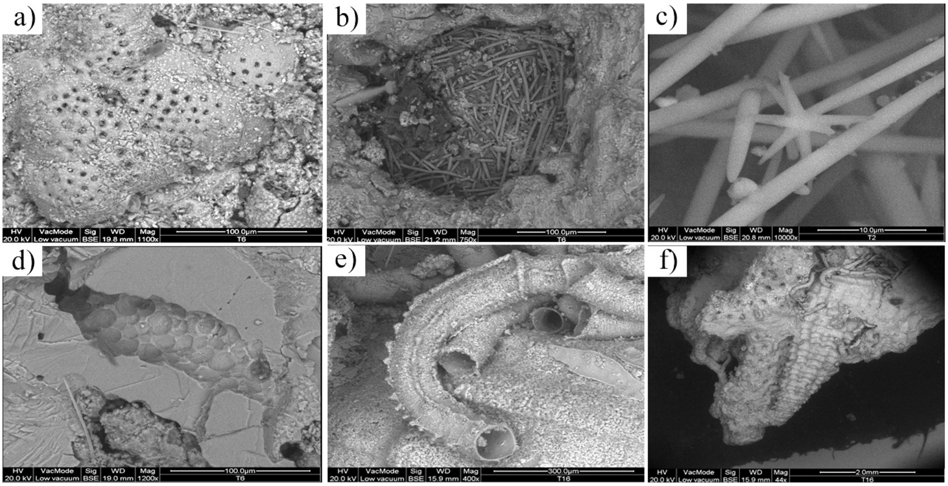

Figure 4. SE-SEM images of the superficial layer of the samples; a) Deposits related to bryozoans; b) Skeletal elements of endolithic sponges, oxeas; c) Tylostyles of excavating sponges and spiraster of epilithic sponges; d) Excavating patterns of endolithic sponges; e) Superficial aggregation of serpulids; f) Gastropod with serpulids.

Alteration mechanisms and the extent of decay affecting the samples can be observed in Figure 3c, with the various types of micro-cracks due to biological activity particularly visible. The marble surfaces showed superficial patinas; the latter's thickness ranged between 20 microns and 5 mm and were not always firmly attached to the stone. However, observations of patina–stone contact revealed continuity between the two, while the former was homogeneous and just one layer was observed. Patina percolation into the substrate of up to about 0.2 mm was obvious at several points. Superficial disaggregation of marble was also clear (Figure 3c).

Morphological observations carried out via SEM enabled characterisation of the biological colonisation present on the substrate. The surface of sample T2 exhibited deposits associated with bryozoan activity (Figure 4a), while it was also possible to recognise skeletal elements of endolithic

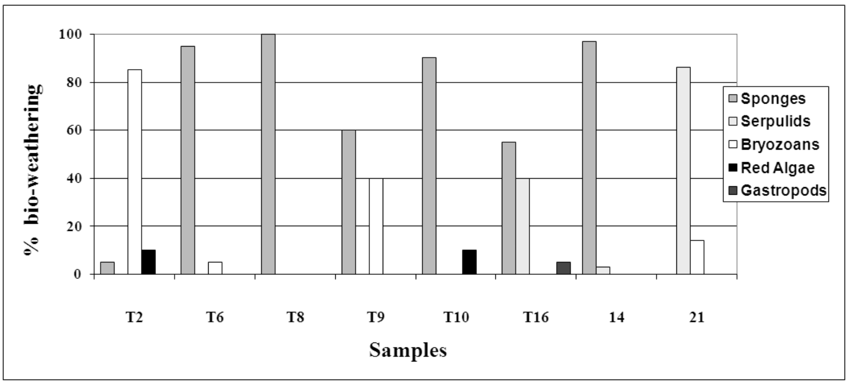

Figure 5. Assessment of biological colonization on each sample.

Table 1: MGS, Mn and isotope analyses of four representative samples from the statue and the stony base.

Sample	Sampling (mm)	MGS	$^{87}Sr/^{86}Sr$	Mn (ppm)	$\delta^{13}C$ ‰ PDB	$\delta^{18}O$ ‰ PDB
T6	Statue	0.8	0.7079	66	2.2	-1.3
T14	Statue	0.8	0.7077	69	2.1	-1.6
B1	Base	0.8	0.7077	68	2.2	-1.4
B2	Base	0.8	0.7078	71	2.4	-1.7

sponges, including oxeas spicules and tylostyles (Hooper and Van Soest, 2002) more than 100 µm in length (Figure 4b,c). A number of encrustations due to coralline red algae were also present.

Some samples were characterised by the excavation patterns of endolithic sponges, including pits resulting from bioeroding activity (Figure 4d), as well as superficial aggregation of serpulids (Figure 4e); the presence of calcareous deposits, corals and gastropods was also detected (Figure 4f).

These results highlight that the main cause of stone decay in underwater environments is typically related to sponge activity (Calcinai et al., 2003; 2004), with the latter's pitting and boring particularly destructive. In contrast, both serpulids and bryozoans are fouling organisms which may play a 'bioprotective' role on colonised surfaces (Ricci et al., 2009); such animals cannot be defined as true bioweathering agents, but rather lead to 'aesthetic' alteration. A semi-quantitative assessment of biological colonisation on each sample is summarised in Figure 5.

Microscopic analysis enabled an evaluation of the maximum grain size (MGS) of calcite grains to be carried out (Table 1), data which represent an important diagnostic parameter when determining the provenance of marbles (Moens et al., 1988). Very similar MGS values were found within all samples, with around 0.8 mm recorded for both statue and base. As the diagram in Figure 6 illustrates (Gorgoni et al., 2002), this value lies in the compositional fields associated with the marble sources of Carrara, Docimium

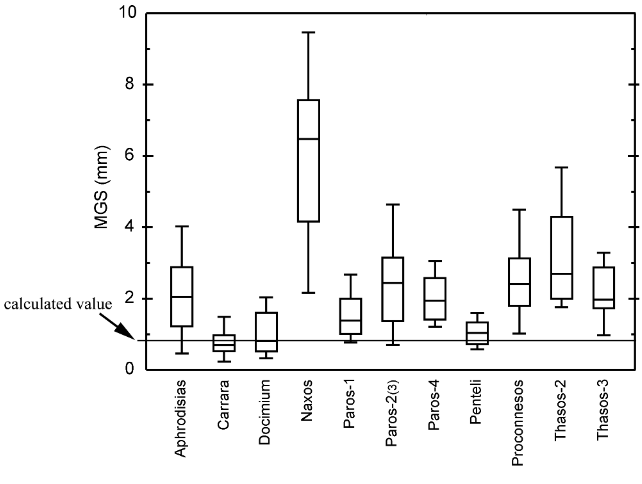

Figure 6. Maximum grain size diagram of Mediterranean marbles by Gorgoni et al., 2002.

(Afyon), Penteli (Pentelikon), Aphrodisias and Paros.

Mean Mn content values obtained via LA-ICP-MS and plotted in Figure 7 (Moens et al., 1988) are similar to those of a wide range of marble sources, with the data compatible with the Carrara, Afyon, Naxos and Thassos quarries. In terms of carbon and oxygen isotopic values, fresh and weathered material differ by up to around 0.6‰; although unaltered marble was selected for provenance analysis in the present study, interaction between the underwater environment and marble that could lead to misleading results cannot be excluded. This fact confirms the necessity of combining a variety of different techniques (Table 1).

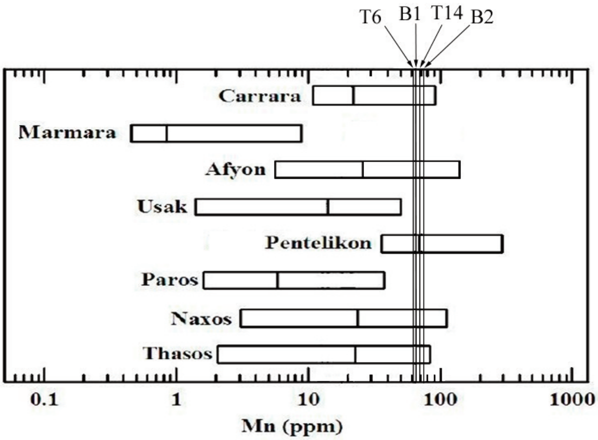

Figure 7. Mn content diagram of Mediterranean marbles, by Moens et al., 1988, vertical lines correspond to the obtained results in this research.

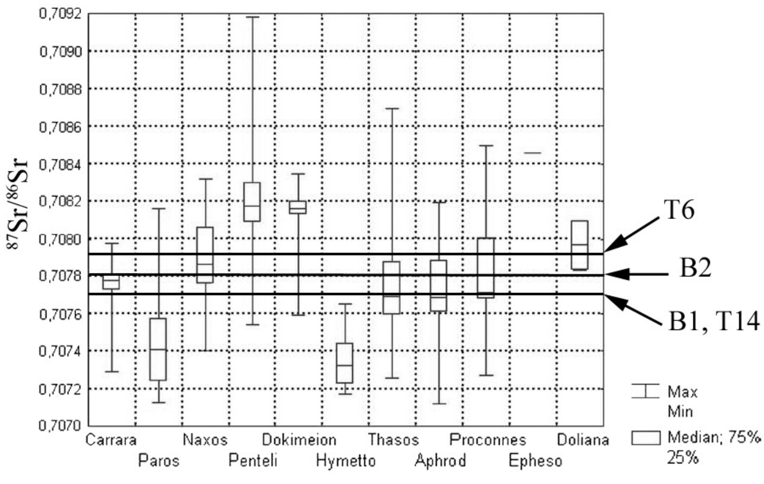

Figure 8. $^{87}Sr/^{86}Sr$ ratios diagram of Mediterranean marbles, Brilli et al., 2005, vertical lines correspond to the obtained results in this research.

Herz et al. (1982) observed that strontium isotopic composition appeared to vary significantly between marbles from quarries located in different Mediterranean regions, and thus analysis of such data was suitable for marble provenance purposes. The values obtained here for the marble samples were compared with a plot of known Mediterranean marble $^{87}Sr/^{86}Sr$ ratios, as shown in Figure 8 (Brilli et al., 2005). However, any potential assignment of material source is mostly unclear, with only Hymetto able to be excluded (Table 1).

Plotting the Grotta Azzurra marble samples on the bivariate plot of C and O stable isotopes presented in Figure 9a (Moens et al., 1992; Gorgoni et al., 2002) results in superimposition with a variety of different sources. However, since the present samples exhibited an MGS value < 2 mm, it was then possible to employ a bivariate plot referring to only fine grain marbles (Gorgoni et al., 2002) (Figure 9b). This second plot reveals that the samples fall into the intersection area of the Carrara and Hymetto sources; since the latter was excluded after strontium isotope analysis, a Carrara provenance for the Grotta Azzurra artefacts is very likely. Moreover, according to the whole data set it is clear that the two stony materials are very similar, thus confirming the same origin of the statue and its base (Table 1). These results are in

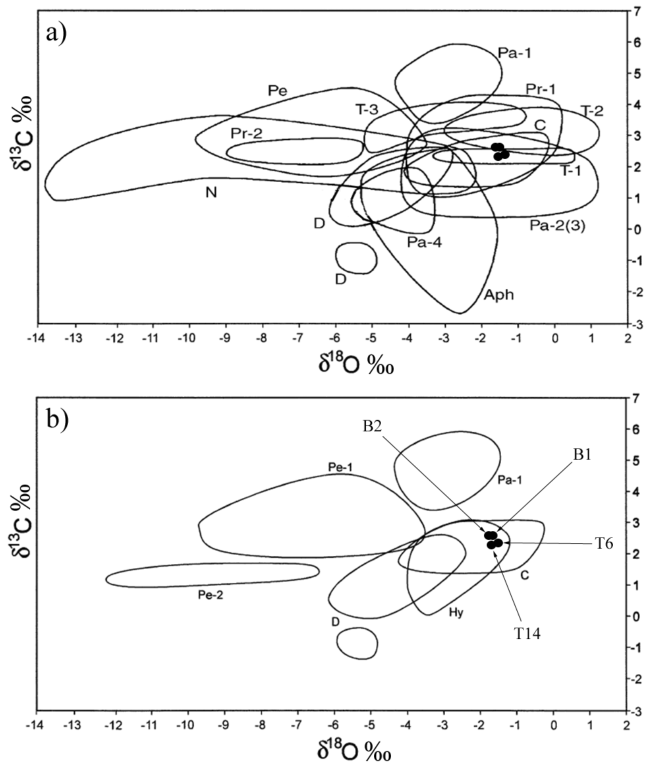

Figure 9. C and O stable isotope diagram of Mediterranean marbles; C = Carrara, Hy = Hymetto, Pe-1 and Pe-2 = Penteli, Pa-1 = Paros, D = Dokimeion; a) General chart, Moens et al., 1988 and modified by Gorgoni et al., 2002; b) Fine grained (MGS < 2 mm) chart Gorgoni et al., 2002.

accordance with the literature, with previous research also pointing to Carrara as the provenance of similar marble artefacts from Campania (Davidde et al., 2010).

Conclusions

In this study a multidisciplinary investigation was carried out in order to determine the sculpture material characteristics and state of preservation of a marble statue representing a *Tritone Barbato*, together with another assumed to be its base. Both items were found in an underwater environment on the island of Capri, southern Italy.

Optical and scanning electron microscopy suggests that the materials have suffered from several forms of biological colonisation, likely attributable to epilithic and endolithic species, particularly boring sponges, which has led to evident stone decay. The activity of other species such as serpulids and bryozoans has resulted in unaesthetic encrustations.

Marble provenance is often problematic, with each available technique potentially providing non-confirmatory results. In the present study a variety of methods were thus employed, including assessment of maximum grain size, Mn content, as well as stable strontium, carbon and oxygen isotopic ratios. The use of this combination of techniques has led to the conclusion that the two marble items found in the Grotta Azzurra in Capri were probably sourced from a Carrara quarry, while their very similar mineralogical, petrographic and geochemical characteristics suggest that the monolith is likely the statue base.

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